

Asymmetry in Methyl Group of Ethane During Internal Rotation: *Ab Initio* Study

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ABSTRACT: Computational studies of the minimum energy pathway for internal rotation of a methyl group are often made by constraining one dihedral angle at a sequence of values and optimizing all other parameters. When this is done, the methyl group adopts an asymmetric configuration at intermediate values of the torsion angle, with unequal bond lengths, bond angles, and torsion angles, even though the moiety against which it is rotating is another methyl group. The potential surface leading to this phenomenon is investigated using Hartree–Fock SCF calculations at the 6-31G* and 6-311G** levels and the detailed structural behavior of the methyl group during the course of the internal rotation is examined. It is shown that the nature of the constraint governs the resulting deformation of the methyl group symmetry. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1141–1145, 1998

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Introduction

In experimental studies of the geometry of molecules that undergo internal rotation, the methyl group is frequently treated as a rigid symmetric rotor with local C_{3v} symmetry. However,

there is extensive evidence, both experimental and computational, that this is not generally valid when the group to which the methyl group is attached is not also three-fold symmetric.^{1–10} The information that has accumulated may be summarized by the following statement: *The local symmetry of a methyl group within a molecule depends on the overall symmetry of the molecule.* This means that the local symmetry of the methyl group will be as asymmetric as the overall symmetry of the molecule allows it to be. The statement just expressed refers to molecules in their equilibrium state, thus an obvious question arises as to whether it is still valid for

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a molecule that is not in a stationary state, for instance, during internal rotation.

In 1982, Burkert and Allinger published an excellent study¹¹ in which they showed that the methyl group in ethane loses its threefold symmetry axis when driving one torsion angle from 60° to the eclipsed value of 0°. The calculations were carried out with the MM2 force field. Later, using *ab initio*, methods we found a similar phenomenon not only for ethane itself but also for several ethane-like molecules.¹² The purpose of the present study is to compare, in more detail, the results of molecular mechanics¹¹ and *ab initio* calculations.

Computational Details

The geometries were fully optimized at the Hartree-Fock level of theory, using the GAUSS-92 program package.¹³ Two series of calculations at different levels of theory have been performed: (1) The 6-311G** basis set was used to characterize asymmetry of the methyl group in ethane while driving one H—C—C—H torsion angle and optimizing the remaining 17 parameters at each increment; this is called the "asymmetric model." Then, the energy differences between the asymmetric and the "symmetric model" were calculated optimizing the structures with constrained C_{3v} symmetry for the methyl groups. (2) The 6-31G* basis set was used to study qualitatively the shape of the potential energy surface in the vicinity of the central point where all the effects, both energetic and geometric, are maximized.

Results and Discussion

The conformational energy surface for internal rotation in ethane can be considered by reference to Figure 1a which reproduces Figure 1 from the work by Burkert and Allinger¹¹ with the addition of three straight lines, *A*, *B*, and *C*, passing along paths of interest (for our discussion). The point at which all torsion angles are equal to 0° represents the higher-energy, eclipsed configuration (i.e., our starting point). If the torsion angles are allowed to vary, but subject to the condition that $\omega_{14} = \omega_{25} = \omega_{36}$ (i.e., the methyl groups retain their internal C_{3v} symmetry), the system follows the path shown by the dashed line in Figure 1a, moving down to the minimum energy staggered conformation in complete accord with the formulation of the reaction coordinate given by Fukui.¹⁴ If, on the other hand, motion away from the eclipsed conformation is driven by the procedure that one torsion angle, say ω_{14} , is set equal to a series of progressively larger values from 0° to 60°, the system will follow the solid line in Figure 1a rather than the dashed line.

The effect of driving a single torsion angle is illustrated by calculations at the 6-311G** level, with the results shown in Table I.

The two methyl groups retain identical structures during this driven motion, maintaining the C_2 overall symmetry of the molecule, but internally they lose all their symmetry, regaining it when they reach the staggered conformation. A similar phenomenon was noted in an *ab initio*

TABLE I.
Optimized Geometries of CH₃ Groups in Ethane at HF/6-311G** Level with Only One Torsion Angle, $\omega(H_1-C-C-H_4)$, Fixed at Various Intermediate Values.^a

(H ₁ —C—C—H ₄)	Eclipsed 0°	15°	30°	45°	Staggered 60°
(Other two) ^b	0°	17.71°	33.54°	47.34°	60°
C—H ₁	1.08514	1.08528	1.08563	1.08601	1.08621
C—H ₂	1.08514	1.08474	1.08498	1.08558	1.08621
C—H ₃	1.08514	1.08597	1.08660	1.08666	1.08621
∠C—C—H ₁	111.636	111.553	111.362	111.201	111.191
∠C—C—H ₂	111.636	111.918	111.879	111.584	111.191
∠C—C—H ₃	111.636	111.211	110.948	110.959	111.191
Δ <i>E</i> (cal / mol) ^c	0.0	50.0	95.0	42.0	0.0

^a Distances in angstroms, angles in degrees.

^b These two torsion angles were optimized independently and were found to be identical.

^c Δ*E* is the energy difference between the quoted structures and symmetrical structures in which all dihedral angles are fixed at the values shown in the caption, *not* the difference from the staggered minimum.

study of acetaldehyde by Ozkabak and Goodman¹⁵ (see their Table III). However, due to the lower symmetry of their molecule, the two torsion angles not driven are no longer identical, the highest difference between them being 6.16° . The energy differences between the structures shown and those in which all three dihedral angles are fixed at the values shown in the column captions (corresponding to local C_{3v} symmetry) are shown in the bottom row of Table I to amount to nearly 100 cal mol^{-1} . A direct demonstration of the higher stability of the asymmetric model is achieved by optimizing the originally symmetric model (point 1 in Fig. 1a) with one torsion angle fixed that converges to point 2. (Note that the GAUSSIAN program cannot break the symmetry in the starting model. However, making a minute change to one of the six C—H distances, from 1.08560 \AA to 1.08561 \AA , permitted the program to converge.) Generally, the asymmetric model is energetically favored over the symmetric one, but the opposite is true for just two points where the torsion angles are equal to 0° and 60° . This means that, even if one torsion angle is fixed at the eclipsed value of 0° , then the asymmetric starting model converges to the symmetric one.

As mentioned previously, Figure 1a was obtained by empirical calculations at the MM2 level.¹¹ To be certain that the general contours are preserved in *ab initio* calculations, in Figure 1b we have plotted energies along the paths marked B and C. It can be observed that the minimum along path B is at 30° , whereas along path C it is in the neighborhood of 33° , perhaps a shade less than would be read off the molecular mechanics plot, but still emphasizing the same overall topography. From these data, it is evident that the energy profile associated with movement along path A must quantitatively look the same as that for path C.

An understanding of the reason for the asymmetric character of the methyl groups at intermediate values of the torsion angles can be achieved by consideration of the interactions between hydrogen atoms on the two methyl groups. In the equilibrium staggered conformation with overall D_{3d} symmetry, each hydrogen atom (e.g., the one marked with an asterisk in the diagram below) is subject to one anti and two skew interactions from the hydrogen atoms on the opposite carbon. In the transition state form with overall D_{3h} symmetry, each hydrogen is affected by one syn and two gauche interactions. However, at intermediate an-

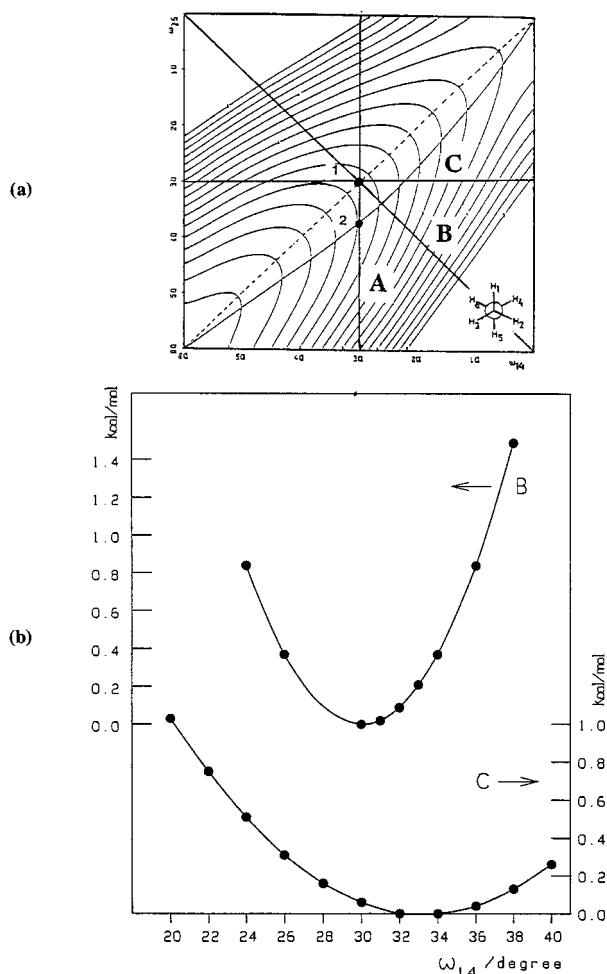
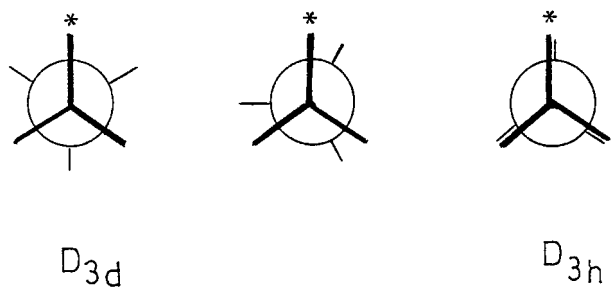


FIGURE 1. (a) Conformational energy map and reaction pathways for internal rotation in ethane obtained with the MM2 force field.¹¹ The contours of total steric energies are spaced at 0.25 kcal/mol . The vertical line, A, is a tangent to the energy contour at point 2 and intersects the dashed line, which corresponds to symmetric methyl groups. Line B is perpendicular to the dashed line. Line C is horizontal and corresponds to ω_{25} fixed at 30° . (b) Energies calculated at the 6-31G* level along lines B and C passing through point 1 of Figure 1(a). All parameters except the two constrained dihedral angles are optimized. The least-square fit to the curve, which corresponds to line C is $E (\text{kcal/mol}) = 6.02 \times 10^{-6}x^3 + 5.30332 \times 10^{-3}x^2 - 0.3735548x + 6.33362305$, where $x = \omega_{14}$.

gles, each hydrogen atom is in an asymmetric environment with one near-syn, one near-gauche, and one near-skew interaction.

It was recognized long ago that steric interactions are important in determining the torsion energy function.¹⁶ In Figure 2 we have plotted the nonbonded distances between hydrogen atoms.



The solid line corresponds to the symmetric model, whereas the dashed lines show the nonbonded $H \cdots H$ distances when the motion is driven by imposed variations of ω_{14} . The resulting distortions of the bond distances and angles permit the other two pairs of opposing hydrogen atoms to maintain a slightly greater separation from each other. Note that two nonbonded $H \cdots H$ distances, $5 \cdots 8$ and $6 \cdots 7$, are refined to be identical exactly like the corresponding torsional angles ω_{58} and ω_{67} . It happens, however, when the methyl group itself is totally asymmetric, having three different C—H distances and C—C—H bond angles (see Table I). Logically, the $H \cdots H$ distances for the

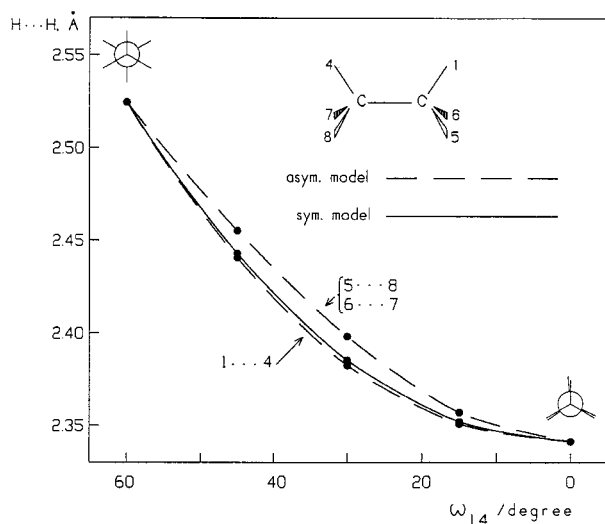


FIGURE 2. Nonbonded $H \cdots H$ distances as a function of torsion angle. The solid line shows results when all torsion angles are constrained to be identical. The dashed lines show the difference between two groups of hydrogens when only one torsion angle is driven. Note that the numbering of hydrogen atoms adopted here is different from that in Figure 1a.

symmetrical model fall in between. From this we may infer that these models are governed by a principle of mutual avoidance of the hydrogen atoms.

The asymmetry of the methyl groups in ethane during the course of internal rotation, which is driven by forced changes in only one torsion angle, follows a rule that appears to be quite general for static structures: When a methyl group is attached to a moiety of lower symmetry, the methyl group distorts to adopt the symmetry of the other group. As one of many illustrations, in $CH_3-NHC_2H_4NH_2$, the methyl group distorts to match the C_1 symmetry of the $-NHC_2H_4NH_2$ group (the C—H distances are 1.089, 1.0911, and 1.0830 Å).⁵

Structural chemistry provides several examples that can be viewed as logical consequences of a model of the asymmetric group. For instance, the methylene group may be viewed as a methyl group with one hydrogen atom substituted by a carbon atom leading to a structure having a constrained adjacent bond angle. With this distortion of symmetry, the two C—H distances are no longer required to be equivalent. This expectation is confirmed in the structure of cyclohexane, $(CH_2)_6$, where the axial C—H bonds are found to be *longer* than the equatorial C—H bonds.¹⁷ The same is found in the methylene group structures in trimethylene sulfoxide.¹⁸ Similarly, the PH_2 group can be viewed as an AH_3 group in which one of the hydrogen atoms is replaced by a lone pair. With the same reasoning as before, it is no surprise to find that, in P_2H_4 , there are two different values for the P—H bond lengths and bond angles.¹⁹

The nonequivalence of CH_2 and PH_2 bonds just cited arises from static rather than dynamic causes. However, a recent experimental study of H_2O_2 and H_2S_2 by Pelz et al.²⁰ has experimentally shown the torsional dependence of the S—S and O—O distances and of the H—O—O and H—S—S bond angles by analyzing the rotational constants of excited states. The torsional dependence of these molecules is in good agreement with our previously calculated values.¹² It is important to mention here that for both this and the previous example with diphosphine, the torsion angle driving method that we used earlier in *ab initio* calculations^{21,22} gives the correct answer. This observation perhaps implies that the asymmetry of the methyl group discussed in this work may be real, not an artifact of the computational procedure used.

Conclusions

Our *ab initio* calculations at the 6-311G** level of theory confirm the previous molecular mechanics results concerning the shape of the internal rotation potential energy surface in ethane. This surface has an interesting feature: If the process of internal rotation starts from a perfectly symmetrical eclipsed conformation it follows the minimum energy reaction path of steepest descent toward the staggered conformation. If it is stopped at a certain intermediate point, and just one torsion H—C—C—H angle is constrained, then the molecule glides to an adjacent minimum that is only 40–90 cal/mol deeper. In this minimum, however, the individual methyl groups completely lose their symmetry while maintaining the overall C_2 symmetry of the molecule. This is achieved by an appropriate combination of the H···H non-bonded distances, which is in accord with the principle of mutual avoidance of the hydrogen atoms.

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